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ELECTRIC CONDUCTIVITY OF WATER EXTRACTS FROM SOIL AS A MEASURE OF THEIR IONIC STRENGTH

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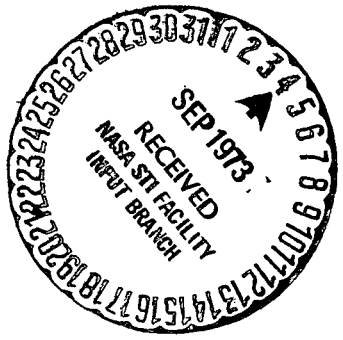

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16. Abstract This paper discusses the problem of determining ionic activity relative to the activity coefficient f in water extracts of soil. The activity coefficients are today calculated usually by the Debye-Huckel formula, in which the ionic strength remains, after the admissible simplification, the only independent variable. It is calculated from analytical concentrations, which takes much time and work. The measurement of the electric conductivity is simple and fast, and correlates well with ionic strength. Experiments were made with synthetic solutions and with soil water extracts using the results from greenhouse experiments. The limits of the method were also determined with regard to the pH value of the solution

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ELECTRIC CONDUCTIVITY OF WATER EXTRACTS FROM SOIL AS A MEASURE OF THEIR IONIC STRENGTH

S. Crnogorac

Introduction

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To determine ionic activity for the purpose of determining the limiting potential of some elements in the soil, the Debye-Huckel formulas

$$-\log f_i = A \cdot z^2 \cdot \sqrt{I} \quad \text{for } I = 10^{-2} \text{ and} \tag{1}$$

$$-\log f_i = \frac{A \cdot z^2 \cdot \sqrt{I}}{1 + \sqrt{I}} \quad \text{for } I = 10^{-2} \text{ to } 10^{-1} \tag{1a}$$

are used, where f_i is the mean ionic activty coefficient, z is its valence, I is the ionic strength of the solution and A is a constant which depends on the dielectric constant of the solution and the temperature, whose value is approximately 0.51 at 25°C of the water solution.

The above formulas give the activity coefficient as a function of ionic strength. The latter is calculated from the analytic cation and anion concentration. The value is:

$$I = 1/2 \Sigma c_i z_i^2 \tag{2}$$

where c_i is the molar concentration of the i-th ion. Because it is difficult to determine all anions in the expression instead of the cation, the equivalent amount of univalent chlorine ion is substituted (Ulrich 1961). When I is known, f can

* Numbers in the margin indicate pagination in the foreign text.

be calculated (Ulrich 1961). The diagram gives the dependence of f on uni-, bi- and trivalent ions for the two roots of I from which the value for f are easily determined. Hence, the activity is

$$a = c \cdot f. \qquad (3)$$

A considerable part of the determined activity passes naturally through the aforementioned region. According to Mengel (1965), it is the ionic activity, not its concentration which is the important quantity for plant nutrition. Further, all formulas for the ionic changes in a reaction on a ZDM base require that the activity be substituted instead of the concentration, and also all other physical-chemical characteristics of the soil, development of the profile, loss of nutrients due to ablution, ion fixation in an unalterable form are intimately related to ionic activity (Wiklander, 1964). /128

As was mentioned above, it is important to determine ionic activity simply and eventually improve it in the future.

Attempts were made to measure cation activity directly electrometrically (Shuffelen and Loosjes, 1952) among the remaining cations and on separately arranged electrodes, (Marshall (1950), Peech and Scott (1950)), in analogy with the widely used method for determining the activity of a hydrogen ion by the pH. These attempts, so far, have yielded limited results. Given the present day state of research, the method according to Debye-Huckel, as presented above, is most reliable. For practical application, they should be compared. That is to say, to determine all or at least most ionic layers in the water extracts from the soil is very time-consuming, and we are often only interested in the activity of one or two ions.

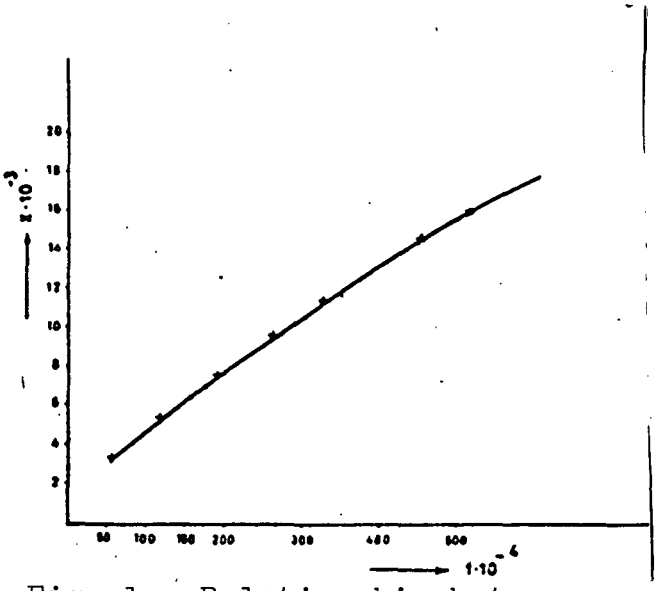

Fig. 1. Relationship between electric conductivity and ionic strength of solutions.

Material and Method

For a solution of constant composition, the electroconductivity is directly proportional to the total ionic concentration and it also depends on the ionic strength. Fig. 1, which gives the dependence of the conductivity on the ionic strength in a synthetic solution of constant composition and various absolute concentrations, shows this proportionality. The composition and concentration of these solutions were selected in such a way that they correspond to the liquid phase of soil in natural conditions. In them are represented all most important ions which are found in agricultural arable soils, namely Ca, Mg, K, Na, HCO_3, Cl, SO_4, NO_3 and PO_4.

The ionic strength I is calculated from the known concentration of the solution by formula (2).

The electroconductivity is measured by a Mullard conductometer which has a thermometer and a scale for temperature correction, which was not needed in our case. Since the total conductivity of the solution is obtained from the ionic conductivity of the individual components, a change in the individual components leads to a change in the constant concentration and a different conductivity. For the time being, for our special case, the method is sufficient and reliable, and the limit is given below. Table 1 gives the ionic conductivities of some of the ions which interested us.

TABLE 1. IONIC CONDUCTIVITY OF SOME IONS AT 25°C IN $ohm^{-1}\ cm^2\ g \cdot ion^{-1}$

CATION	l_0	ANION	l_0
H	349.82	OH	198
K	73.52	Cl	76,34
NH_4	73.4	NO_3	71,44
1/2 Ca	59.50	1/2 SO_4	79,8
1,2 Mg	53,06	HCO_3	44,48
Na	50,11	CH_3COO	40,9

The above table gives the ionic conductivities which interest /129
us, except H and OH, in which the variations that are close to their own in some constant total concentration are measured, even if in wider boundaries it is not possible to bring about a substantial difference in the total conductivity.

For solutions in which the concentration of the H and OH ions is high, which can be seen from their ionic conductivity, the above conductivity is no longer proportional to the concentration.

In the subsoil, the conductivity used to determine ionic strength probably lies only in the pH interval between the values 5 to 9, because in this interval the ratio of the ionic conductivity of the H and OH ion, on account of their small concentration, is negligible. Fortunately, the pH values of water extracts of most cultivated soils lie in this interval.

To verify what has been said above, an attempt was made to determine the ionic strength of one from among the others versus conductivity in the aqueous soil extract in order to set up the manure pot experiments of Crnogorac (1964). This experiment has 20 ions and, after four repetitions, the water soil extracts had a different composition and their pH fluctuated from 5.8 to 6.5. The water extracts were obtained in the following manner: 20 ml /130
of distilled water is added to 30 g of the soil, and the mixture is mixed. Through this suspension, nitrogen is passed through

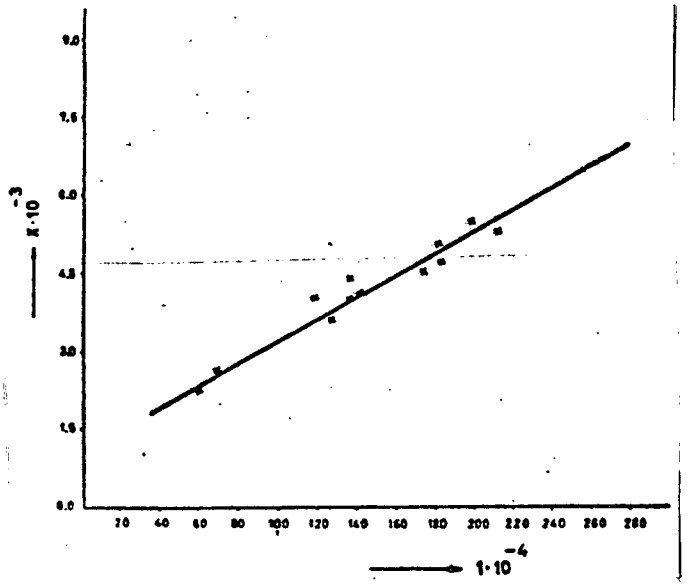

Fig. 2. Relationship between the electric conductivity of the water extracts of the soils and its ionic strength.

the entire flask for a period of 15 min while it is mixed. Then the suspension is centrifuged to 16,000 rpm and the water phase is decanted. The electric conductivity is determined in this solution with the aid of a standard conductometer, and also the Na, K, Ca, and Mg concentration is determined with a flamephotometer and the Na, K, Ca concentration with a spectrometer (Mg). From these concentrations, when they are recalculated into molar values, the ionic strength I is obtained. Fig. 2 shows the relation between the electroconductivity and the ionic strength I.

Conclusion

With the aid of simple and fast measurements of the electroconductivity, it is possible to calculate the ionic strength of a soil water extract. This eliminates the determination of the ions present, and the calculations of the ionic strength I.

The condition for applicability is that the pH extract be between the limits from 5 to 9.

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